

**INSULATION PRODUCT, ESPECIALLY THERMAL INSULATION
PRODUCT, AND ITS MANUFACTURING PROCESS**

5 The invention relates to the use of a novel type of
synthetic resin for producing mineral-fiber-based
products that can be used at high temperature (above
150°C, especially 200 to 500°C, or even up to 700°C and
higher for certain mineral fibers), especially those
10 based on glass fibers or rock fibers, such as for
example mineral fiber mats intended for thermal and/or
acoustic insulation of buildings or equipment.

Most insulating materials based on mineral fibers
15 include a binder that ensures mechanical integrity of
the material, that is to say binds the fibers together.
This binder must be dispersed uniformly over the fibers
in order to prevent the formation of fiber islands
surrounded by a binder gangue in a collection of fibers
20 that are unbonded, more brittle and therefore generate
more dust.

It is known to use phenoplast (phenol-formaldehyde) or
aminoplast (melamine-formaldehyde or urea-formaldehyde)
25 thermosetting resins. The resins most commonly used are
resols, namely products of the condensation, in the
presence of alkali metal or alkaline-earth metal
catalysts, of phenols carrying vacant ortho and para
positions and aldehydes (mainly formaldehyde). These
30 resins are used in a sizing composition that also
contains water, as dilution agent, urea, that serves to
reduce the amount of free formaldehyde and also acts as
a binder, and various additives such as oil, aqueous
ammonia, colorants and possibly fillers.

35 For applications in which the mineral-fiber-based
product may be subjected to high temperatures,
especially above 150°C, in particular above 200°C, or
even above 300°C and even sometimes above 400°C,

conventional phenoplast-type binders are unsatisfactory as they decompose and generate gaseous emissions that may be undesirable, especially formaldehyde, methyl isocyanate (denoted hereafter by MIC) and/or isocyanic acid (denoted hereafter by ICA) and/or other volatile organic compounds (denoted hereafter by VOC). In fact, MIC and ICA emissions start to be detected above 150°C and become significant beyond 200°C when products manufactured with conventional phenoplast-type binders are heated.

To reduce MIC emissions with phenoplast-type resins, it has been proposed to use sizing compositions based on a phenol-formaldehyde resin substantially free of urea or of urea derivatives, as the Applicant has described in European patent application EP 1 022 263. This solution makes it possible for the MIC emissions liable to occur when the product is heated to be very substantially reduced, but is not completely satisfactory as it results in inferior trapping of the formaldehyde emitted during manufacture of the product compared with a conventional sizing composition (for example of the type of those described in the Applicant's patent EP 0 480 778).

Another means for solving the problem of emissions is known and consists in using mineral binders instead of binders based on organic resins. These mineral binders advantageously solve the problem of undesirable gas emission up to 500°C, or even up to 700°C, but have considerable drawbacks that limit their use. Binders based on aluminum phosphate are suitable for this use, especially those sold by the Italian company Poletto under the brand name LEGAREFF.

Firstly, such products are sometimes difficult to manufacture as it is noted that there is a significant

tendency of bonding to the line, especially to the conveyor belts.

Secondly, the mechanical quality of the insulating product obtained with such binders is very inferior to that of products obtained with phenoplast binders. This is because it is noted that the mineral binder is sensitive to moisture and it is frequently observed that the product swells during its storage. Furthermore, substantial delamination is observed in the product and there are risks of part of the product being torn off during handling.

It should be pointed out that applications of fibrous insulation capable of withstanding the high temperatures mentioned occur, for example, in the oven (especially domestic electric oven) field, the lagging field (especially the lagging of pipes in which the insulation is used in the form of a shell), the fire protection field (for example fire doors), the transportation field and the nuclear field.

It is apparent that, to produce end products, such applications require steps of handling, shaping and adjustment of the insulating products used.

The use of insulating products comprising a mineral binder results in much more difficult processing than with insulating products comprising a binder based on an organic resin, and often results in high scrap rates.

It is an object of the invention to select a type of synthetic organic resin for producing mineral-fiber-based products, said product being able to be used above 150°C, especially between 200 and 500° or even up to 700°C and higher in the case of rock fibers, while considerably reducing undesirable gas

emission compared with the known solutions of the prior art.

It should be noted that the use of insulating products
5 based on glass fibers, especially those having a
soda-lime borosilicate composition, is limited to
temperatures of about 500°C, whereas it is possible to
use rock-fiber-based products, which in general
comprise a low content of alkali metals, up to 750°C or
10 indeed at even higher temperatures.

There are a very large number of criteria for selecting
a binder, and these fall within various categories;
however, it should not be forgotten that a binder must
15 above all adhere to the glass correctly.

Firstly, it is essential for the binder to be
rheologically compatible with the fiber manufacturing
process. Without entering into details that are
20 irrelevant here, we point out that glass fibers are
usually produced by means of a spinner whose axis is
oriented vertically and into which a continuous stream
of molten glass is introduced. The glass is thrown
against the peripheral wall of the spinner, from which
25 it escapes in the form of filaments via a very large
number of small holes, said filaments being attenuated
and carried away downward by means of a high-
temperature, high-pressure gas stream. The fibers
obtained are collected on a gas-permeable conveyor and
30 thus form a blanket of greater or lesser thickness
depending on the speed of the conveyor. In the case of
rock fibers, the fibers are usually produced with a
spinner having a horizontal axis.

35 The sizing composition must be distributed over the
fiber thus produced, in order thereafter to preferably
be located at the junction points between fibers and to
allow an elastic fibrous blanket to be obtained; it is

therefore preferable to spray the sizing composition while the fibers are still individual fibers, that is to say before the blanket forms. Consequently, the sizing composition is sprayed into the fiber collection
5 hopper, beneath the burners that generate the gas attenuation stream. The corollary of this option is to preclude the use of inflammable and/or contaminating organic solvents for the formulation of the sizing composition, the risk of fire and/or contamination in
10 the collection hopper being too great. In addition, the resin serving as binder must not cure too rapidly before the desired forming operation.

Secondly, although this curing must not be too rapid,
15 it must however not be able to be too lengthy (risk of pre-gelling), since complete curing must be completed in a time compatible with high production rates after residence in a high-temperature oven (at around 250°C).

20 Finally, the resin and its method of use must be relatively inexpensive, compatible with that of fiberizing the glass, and must not lead, directly or indirectly, to the formation of undesirable or contaminating effluents.

25 These objectives are achieved by using a sizing composition, the resin of which consists substantially of at least one epoxy-type resin. The epoxy resins selected by the invention are resins whose EEW value
30 (Epoxy Equivalent Weight, a parameter known to those skilled in the art, corresponding to the weight of resin in grams per mol of epoxy functional group) is between 150 and 2000, preferably at least 160 and/or at most 700, or even at least 170 and/or at most 300. This
35 is because the inventors have demonstrated that these resins advantageously make it possible to obtain very low levels of undesirable gases emitted and are compatible with the known methods for spraying a sizing

composition that are used in the mineral fiber industry for fibers intended for insulation. The thermal and/or acoustic insulation products according to the invention comprise at least 1%, or at least 2% and even more than 5 4% by weight of cured binder from the sizing composition.

Thus, the ease of use of an organic resin (soluble or emulsifiable or dispersible in water and therefore easy 10 to spray) is advantageously obtained. The insulating products manufactured with such resins can be easily handled and shaped. Surprisingly, these products generate no, or very little, undesirable gases during use above 150°C, especially between 200 and 500°C or 15 even up to 700°C and higher in the case of rock fibers.

The term "undesirable gases" is understood to mean especially formaldehyde, MIC, ICA and other volatile organic compounds (VOCs).

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For the purposes of the invention, the amount of gas emitted by a specimen of mineral-fiber-based insulation product comprising a binder and heated to 350°C, especially for at least 15 minutes, preferably 20 25 minutes, in particular 1 hour or more, is characterized, this being representative of the operation of the insulation for the intended applications. This is because it may be considered that, after residing for one hour at 350°C, almost all 30 of the undesirable gases have been emitted. The amount of gas emitted normalized to the weight of product tested is measured. It will be considered that little undesirable gas is emitted if their amount measured in the above test is less than 50 mg/kg, preferably less 35 than 20 mg/kg and even less than 10 mg/kg.

With the resins according to the invention, thermal and/or acoustic insulation products based on mineral

fibers are obtained that can be used above 150°C, especially between 200 and 500°C or even up to 700°C and higher in the case of rock fibers and that comprise at least 1%, or at least 2% and even more than 4% by weight of cured organic resin, while still releasing less than 50 mg/kg (of product), especially less than 20 mg/kg and even less than 15 mg/kg of formaldehyde and less than 50 mg/kg (of product), especially less than 20 mg/kg and even less than 10 mg/kg of methyl isocyanate (MIC) when they are heated to 350°C for at least 15 minutes.

A sizing composition according to the invention is obtained by diluting or emulsifying, in water, a resin or a resin mixture consisting substantially of at least one epoxy resin whose EEW value is between 150 and 2000, preferably at least 160 and/or at most 700, or even at least 170 and/or at most 300, with a nonvolatile amine hardener, and including additives calculated in parts by weight per 100 parts of dry resin. Preferably, 0.1 to 2 parts of silane and/or 0 to 15 parts of a mineral oil, in parts calculated per 100 parts of dry resin, are added.

The amine hardener is especially characterized by the amine/H equivalent weight defined by the MW ratio (molecular weight of the amine to the active hydrogen number). The preferred amines have an amine/H equivalent weight, denoted by "NH number", of between 20 and 300.

Among the epoxy resins of the invention, mention may be made of resins of the glycidyl ether type that are described in the Applicant's European patent EP 0 369 848.

The epoxy resins described in Application EP 0 369 848 are particularly advantageous. In this application,

these resins are described as being beneficial in particular because they do not result, directly or indirectly, in the formation of undesirable or contaminating effluents during fiberizing and the subsequent oven treatments (at about 250°C). However, nothing would have anticipated that such resins could allow the manufacture of products capable of being used above 150°, especially between 200 and 500°C, or even up to 700°C and higher in the case of rock fibers, especially with very low MCI and ICA emissions.

Among epoxy resins of the glycidyl ether type, the following resins, cited with their brand names, have proved to be particularly appropriate:

- resin in emulsion from Resolution: EPIREZ 3510 W60 (EEW = 185 to 215), EPIREZ 3515 W60 (EEW = 225-275) and EPIREZ 3522 W60 (EEW = 615-715);
- resin to be emulsified from Resolution: EPICOTE 828 (EEW = 184 to 190) and EPICOTE 255 (EEW = 193 to 205); and
- resin to be emulsified from Dow Chemical: DER330 (EEW = 176-185) and DER 331 (EEW = 182-192).

Other epoxy resins of the glycidyl ether type are particularly advantageous as they make it possible to give the product improved temperature and fire resistance. These are halogenated glycidyl-ether-type epoxy resins, especially derivatives of dibromophenyl glycidyl ether such as, for example, the following compounds:

- dibromophenyl glycidyl ether, 2-methyl-4,6-dibromophenyl glycidyl ether, 4-methyl-2,6-dibromophenyl glycidyl ether, 2-butyl-4,6-dibromophenyl glycidyl ether, 4-isooctyl-2,6-dibromophenyl glycidyl ether, 2-phenyl-4,6-dibromophenyl glycidyl ether, 4-cumyl-2,6-dibromophenyl glycidyl ether.

Another family of epoxy resins also gives good results: these are novolac epoxy resins such as, for example, the resins EPIREZ 5003-W55 (EEW = 195 to 215).

- 5 It is also possible and advantageous to use a mixture of the epoxy resins described above.

As regards the amine used as hardener, it is possible to use aliphatic, cycloaliphatic or aromatic amines, or
10 imidazoles, polyfunctional hydrazides or dicyandiamides.

As examples according to the invention, mention may be made of:

- 15 - aliphatic amines: diethylenetriamine, triethylenetetramine, tetraethylene pentamine (TEPA), such as EPICURE 3295 from Resolution, polyglycoldiamine and m-xylylenediamine;
- cycloaliphatic amines: 1,3 bis(aminomethyl)-
20 cyclohexane, 4,4-diaminocyclohexylmethane, methanedi-amine and 2,6-diaminocyclohexanols;
- aromatic amines: metaphenylenediamine, diamino-diphenylsulfone and diethyltoluenediamine; and
- imidazoles, such as imidazole, 1-
25 methylimidazole, 2-methylimidazole, 2-undecylimidazole, 2-ethyl-4-methylimidazole and 2-phenylimidazole.

The invention also relates to a thermal and/or acoustic insulation product based on mineral fibers, that can be
30 used above 150°C, especially between 200 and 500°C, or even up to 700°C and higher in the case of rock fibers, comprising at least 1%, or at least 2% and even more than 4% by weight of a binder obtained from a sizing composition, the resin or resin mixture of which
35 consists substantially of at least one epoxy-type resin whose EEW value is between 150 and 2000, preferably at least 160 and/or at most 700, or even at least 170 and/or at most 300.

It should be noted that, after the binder has cured, the epoxy functional groups have reacted during curing and that amine bridges and alcohol functional groups are observed in the binder that coats the fibers.

Furthermore, the product is white if no colorant has been added.

Advantageously, the thermal and/or acoustic insulation product according to the invention furthermore comprises a web of mineral fibers, especially glass fibers, the grammage of which is, for example, between 10 and 300 g/m², placed on at least one of the outer surfaces of said insulating product. Preferably, said web comprises at least 1%, or at least 2% and even more than 4% by weight of a binder obtained from a sizing composition, the resin or resin mixture of which consists substantially of at least one epoxy-type resin whose EEW value is between 150 and 2000, preferably at least 160 and/or at most 700, or even at least 170 and/or at most 300.

Furthermore, the invention also relates to a process for manufacturing a thermal and/or acoustic insulation product based on mineral fibers, especially glass fibers, that can be used above 150°C, especially between 200 and 500°C, or even up to 700°C and higher in the case of rock fibers, which comprises the following steps:

a) preparation of a sizing composition consisting substantially of water, a resin or resin mixture consisting substantially of at least one water-dispersible epoxy resin whose EEW value is between 150 and 2000, preferably at least 160 and/or at most 700, or even at least 170 and/or at most 300, at least one amine hardener and additives (in parts calculated per 100 parts of dry resin), especially between 0.1 and 2%

of silane and especially between 0 and 15% of a mineral oil;

- 5 b) fiberizing, especially by the internal centrifugal process (vertical axis of the spinner, especially for glass fibers) or external centrifugal process (horizontal axis, especially for rock fibers), of a molten mineral composition and spraying of the sizing composition compared in step a) onto the fibers; and
- 10 c) curing of the sizing composition in an oven, especially at around 250°C, in order to form a compressible fiber blanket.

15 In a preferred method of implementing the process according to the invention, the sizing composition of step a) comprises a water-dispersible epoxy resin of the glycidyl ether type and an amine hardener whose flashpoint is above 150°C.

20 Advantageously, in the process according to the invention, at least one aforementioned epoxy resin is a glycidyl ether having a curing index n of less than 1 and preferably less than 0.2.

25 According to another preferred method of implementation, the sizing composition of step a) comprises a water-dispersible epoxy resin of the novolac type.

30 It goes without saying that a mixture of the aforementioned resins lies within the scope of the invention.

35 Preferably, the equivalent molar mass NH of at least one hardener is less than 100 g.

According to a preferred method of implementation, at least one hardener is based on dicyandiamide (DCN).

The invention also relates to the application of the above process to the production of insulating products whose density is between 4 and 200 kg/m³.

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The invention also relates to the use of the product described above and/or manufactured by the above process for insulating walls of objects liable to be heated to temperatures of above 150°C, especially
10 between 200 and 500°C, or even up to 700°C and higher in the case of rock fibers, such as especially walls of ovens, pipes, fire-resistant components, transportation equipment and equipment intended for applications in the nuclear industry.

15

Other features of the invention are explained in detail below with reference to the comparative tests carried out with sizing compositions A, B, C, D, E corresponding to the following formulations (as is
20 usual, the resin and the catalyst or hardener represents 100 parts in the formulation, and the additives are indicated as additional parts).

Comparative examples A, B and C:

25 Sizing composition A:

30	. phenolic resin	80	parts
	. urea	20	parts
	. aminosilane	0.5	part
	. mineral oil	9	parts
30	. ammonium sulfate	3	parts
	. aqueous ammonia (20% solution)	6	parts

The phenolic resin used for sizing composition A is of the type of those described in patent application
35 EP 0 148 050 and corresponds to that used for the manufacture of standard insulation products.

Sizing composition B:

	. phenolic resin	100	parts
	. urea	0	parts
	. aminosilane	0.5	part
5	. mineral oil	9	parts
	. ammonium sulfate	3	parts
	. aqueous ammonia (20% solution)	6	parts

This sizing composition is of the type of those
10 described in EP 1 022 263 (example no. 1).

Sizing composition C:

	. mineral binder based on		
	aluminum phosphate	100	parts
15	. aminosilane	0.5	part
	. oil	9	parts

Examples D and E according to the invention:

20 Sizing composition D:

	. epoxy resin EPIREZ 3510W60 from		
	Resolution	88	parts
	. DCN (dicyandiamide) hardener	12	parts
	. 2,4,6-tris(dimethylaminomethyl)-		
25	phenol accelerator	1	part
	. aminosilane	0.5	part
	. oil	9	parts

Sizing composition E:

30	. epoxy resin: EPIREZ 3510W60 from		
	Resolution	80	parts
	. hardener: TEPA	20	parts
	. aminosilane	0.5	part
	. oil	9	parts

35

Insulation products were manufactured under identical
fiberizing conditions with the above sizing

compositions sprayed so that the products contained 4.5% binder by weight.

The gas emission from these products was measured.

5

The measurement protocol was the following: these sizing compositions were sprayed onto mineral wool fibers, the amount sprayed being the same for all the specimens. A 1 gram sample of each specimen (after the binder had cured) was heated for one hour in a tube furnace at 350°C with an air flow rate of 2 l/min. The amount of methyl isocyanate (MIC) and of ICA conveyed by the air to the outlet of the furnace was measured according to the OSHA No. 54 standard (MIC trapping on a solid trap impregnated with a reactant that picks up MIC and ICA, followed by a safety bubbler containing the same reactant, and finally quantitative determination of the MIC and ICA by HPLC with UV fluorescence detection. The formaldehyde emissions were measured by the amount of formaldehyde given off by an end product heated to 350°C in a tube furnace: 10 g of specimen were placed in the tube furnace at 350°C and a gas stream of reconstituted air was passed through the specimen for one hour; the formaldehyde given off was trapped in two bubblers in series, these being filled with 50 ml of HPLC-quality water; the formaldehyde in each bubbler was measured by the Lange method and the result expressed as formaldehyde (mg) per kg of product. The results of the tests are given in table 1.

30

Table 1

Sizing composition	Formaldehyde in mg/kg of product	MIC (methyldisocyanate) in mg/kg of product	ICA (isocyanic acid) in mg/kg of product
A	60	90	140
B	110	18	20
C	8	2	2
D	8	1.5	10
E	11	2	8

5 It is clearly apparent that the results obtained with the products according to the invention are remarkable and very substantially different from the known prior art with organic binders.

10 This is because the products obtained with sizing composition D or E emit less than 20 mg/kg formaldehyde, less than 10 mg/kg MIC and less than 20 mg/kg ICA, whereas no known phenoplast-based solution allows the formaldehyde emissions to reduced
15 to less than 50 mg/kg and MIC emissions to less than 10 mg/kg.

Results are obtained using the solution of the invention that are entirely equivalent to those
20 obtained with mineral binders (example C) as regards gas emissions.

As mentioned above, the drawback of mineral binders relates to the mechanical properties of the products
25 obtained with such binders - the properties are very much inferior to those obtained with organic binders and they also degrade with wet aging.

To illustrate this point, comparative tests are given in table 2 in which the tensile strength measured after manufacture (TS_{manuf}) and tensile strength measured after an accelerated aging test, consisting in aging the product for 15 minutes in an autoclave whose temperature was 107°C at 100% relative humidity ($TS_{15', \text{autoclave}}$) are indicated for various product densities (about 10 kg/m^3 and 35 kg/m^3).

10

The tensile strengths or parting strengths (TS) were measured according to the ASTM C686-71T standard on ring specimens cut by stamping from a product taken after the curing step.

15

A ring specimen was placed between two cylindrical mandrels of a test machine. One of the mandrels was moved at a constant speed and the force F (in grams force) to break the ring was measured. The tensile strength TS is defined by the ratio F/M , where M is the mass of the specimen (in grams).

20

The ring specimen used was a torus measuring 122 mm in length and 46 mm in width, the radius of curvature of the cut of the outer edge was 38 mm and that of the internal edge 12.5 mm.

25

Table 2

Sizing composition	Density (kg/m^3)	TS_{manuf}	$TS_{15', \text{autoclave}}$
A	11	230	114
A	35	350	175
C	32	160	40
D	12	220	80
D	35	370	140

The results of the mechanical tests prove that, with the products according to the invention (example D), results are obtained that are substantially equivalent (similar, and even sometimes better than) to those with
5 phenophate resins (example A) after manufacture and that remain very satisfactory after an accelerated aging test.

These results show that the mechanical properties of
10 the products according to the invention are greatly superior to those of products manufactured with a mineral binder (example C) after manufacture (a factor of 2 in the results) and after an accelerated aging
test (factors of 3 to 4 in the results).

15